Subcontractor Report

CIS-Type PV Device Fabrication by Novel Techniques

Phase II Annual Technical Report
1 July 1999–30 June 2000

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NREL

National Renewable Energy Laboratory

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1.0 Summary

Thin film solar cells based on CIS-type absorbers show great promise in moving towards commercialization with photoconversion efficiencies approaching 20%. Thus far, the record laboratory efficiencies have been achieved using vacuum-based deposition techniques, the scale-up of which to large areas for high volume production presenting several challenges. Low cost particle coating methods present an interesting alternative to costly vacuum deposition techniques, offering the possibilities of compositional control, high materials utilization and inexpensive deposition over large area substrates. The R&D program at ISET is centered on development of a novel, dispersion based route to the deposition of precursor thin films that are converted to CIS-type absorbers through high temperature reactions at or close to atmospheric pressure.

The goal of the current research program at ISET is to bring a non-vacuum processing route for CIS closer to commercialization by improving the device efficiency through an increase in absorber bandgap. The basic processing approach involves first synthesizing a powder containing the oxides of copper, indium and gallium. A dispersion (ink) is prepared from the starting powder by mechanical milling or sonication. This ink is then deposited onto the glass/moly substrate as a thin precursor (3-4 μm) and converted to a metallic alloy film by reaction in a hydrogen atmosphere. Controlled synthesis of starting powders and proper reduction results in reasonably smooth, metallic precursor films similar to those produced by sputtering or evaporation. From this point the processing is similar to that in the other two-stage techniques, with the metallic film being reacted in H_2Se to form the final photovoltaic absorber, followed by CdS and TCO deposition.

Although CIS efficiencies greater than 12% have been demonstrated using ISET's non-vacuum approach, further increases in efficiency require the addition of gallium or sulfur to raise the bandgap (for CIS, $E_g \approx 1.0$). The inclusion of gallium has been demonstrated to increase the efficiency of solar cells grown by the co-evaporation technique. Higher open circuit voltages are produced when the large bandgap semiconductor CGS is formed near the p-n junction. This bandgap increase has been shown to yield efficiencies of over 18%. In the two-stage process, however, the incorporation of gallium in the bulk of the absorber results in a small grained material and causes poor current collection and low fill factor. Efficiency increase due to gallium inclusion in selenized films is generally limited to a back surface field effect. The gradation in gallium concentration toward the Mo/film interface that generally occurs during selenization can create an electric field to aid in carrier collection deep inside the film and thus improve the current. With this approach sulfur must be incorporated into the active area of the absorber near the junction to increase the bandgap and yield higher open circuit voltages.

During the first year of the Phase II program, work was focused on the following main areas: i) further understanding of sulfur and gallium distributions in films of various compositions, ii) incorporation of sulfur into absorbers produced by the non-vacuum process and iii) fabrication of high efficiency devices and sub-modules. The incorporation of sulfur into CIGS was found to be more favorable in Cu-rich films, aided by the secondary phase of Cu-Se. For gallium diffusion from the back of CIGS films, the

situation is reversed with the diffusion to the front being more favorable for In-rich films, and little gallium diffusion taking place in near stoichiometric films. Using a gallium rich phase at the Mo interface to produce a back surface field, and sulfur at the junction to increase the bandgap, device efficiencies of 13% have been achieved with selenized/sulfurized samples (A<0.1cm^2) from non-vacuum deposited precursors (12.5%, 1-5cm^2). Moly has been successfully laser scribed in house and mini-modules (A<100cm^2) have been fabricated with efficiencies over 8% and Voc's per cell over 480 mV (evidence of increased bandgap).

2.0 Introduction

In order for thin film CIS to realize its potential as a viable photovoltaic material, low cost deposition methods must be found that are capable of producing solar cell quality absorbers over large areas with high yields and high materials utilization. Vacuum growth techniques such as co-evaporation or MBE and two-stage routes such as sputtering or sequential evaporation followed by selenization have proven capable of producing high efficiency devices, but capital equipment costs are high and controlled deposition over large area substrates is difficult. In chalcopyrite materials processing, precise deposition control is crucial to formulating compositions (Cu/(In+Ga) ratios) in the proper range for high efficiency device formation. Particulate routes to CIS precursors address this problem by precisely controlling the atomic ratio at the sub-micron level in the starting powder of dispersion. In this way, the composition is fixed regardless of the deposition method employed, or any local thickness variation that occurs during the formation of the film.

Several efforts have been made at producing solar cell quality CIS by particle deposition techniques. Researchers at Matsushita attempted early on to mix together Cu, In and Se powders in a liquid medium to produce a screen printable paste. During the milling of these powders to reduce the particle size and intimately mix the constituents, it was observed that some of the starting materials reacted to form CIS. This precursor paste was screen printed onto substrates and annealed at high temperature, but the resulting CIS was poorly fused and could not be used for solar cell fabrication. Several research groups have also attempted particulate processing schemes involving the deposition of selenide powders. Recently, researchers at NREL reported the growth of CIGS solar cells from spray deposited Cu-In-Ga-Se nanoparticles[1]. Colloids containing ultrafine powder (10-50nm) were synthesized and sprayed onto glass/moly substrates as precursor films. These mixed selenide powder precursors were then annealed under a high Se flux at 550C and the composition was adjusted to near stoichiometric CIGS by evaporating In and Ga. SEM examination of the final film microstructures showed a fine-grained region that corresponded to the spray deposited powder. Devices were fabricated on absorbers prepared by this powder spraying method but an efficiency of 4.6% was the highest obtained. It was concluded that similar processing must include a step that allows film fusion and grain growth in order to be effective in producing solar cell quality materials.

2.1 ISET's powder processing route to CIGS

The non-vacuum approach to the processing of CIS at ISET has demonstrated solar cell efficiencies over 12% using an inexpensive, dispersion based approach. Rather than starting with metal or selenide powders, oxide powders are synthesized that can be successfully dispersed in water to form a stable ink. Proper synthesis of the powder ensures that the constituent elements (Cu, In and Ga)* are uniformly mixed at an extremely small scale (~10-20nm). Solution processing routes are also capable of producing fine, sub-micron powders, eliminating the need for grinding and milling to reduce the particle size to within the range suitable for thin film deposition (particle diameter < 0.5μm). Figure 1 is an example of the results of a measured particle size distribution for a typical powder synthesized at ISET. The median of the size distribution lies at approximately 250nm. When this powder is mixed in water (with dispersing agents), the composition of the final film is fixed at any point on the substrate. The Cu/(In+Ga) ratio of the CIGS absorber material is uniform despite any irregularities in film thickness that might originate from deposition process employed. Fixing the atomic ratio within the powder eliminates the need to have exacting control over deposition rate and thickness, allowing quick, inexpensive deposition (roll coating, spraying, etc.) to be carried out over extremely large areas (>1m^2) with precise lateral and vertical composition control.

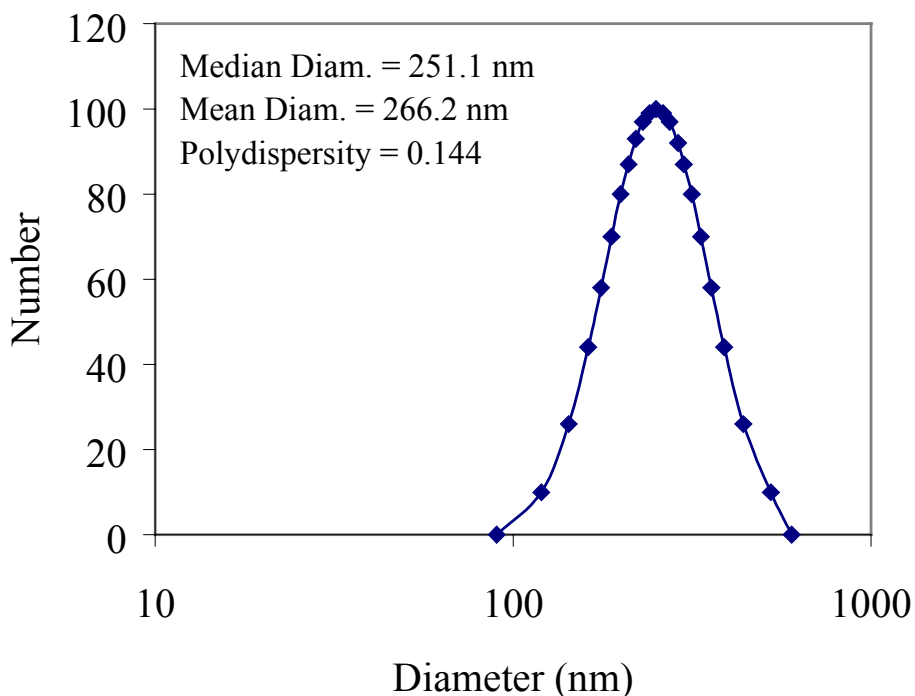Median Diam. = 251.1 nm
Mean Diam. = 266.2 nm
Polydispersity = 0.144

Figure 1). Particle size distribution for standard Cu-In-Ga-O powder synthesized at ISET and used in the formation of CIGS absorber materials.

* Ga inclusion studies are funded through a contract from ATP/NIST

The initial step in the ISET process is the synthesis of oxide powder by co-precipitation, spray pyrolysis, etc., containing the proper ratio of Cu, In and Ga (i.e. Cu/(In+Ga) = 0.94, Ga/(In+Ga) = 0.25). An aqueous ink is formulated from the powder for deposition onto Mo/glass as a precursor film. The surface chemistry of this ink can be controlled by pH adjustment or the additions of various surfactants, dispersants or electrolytes in order to produce the proper rheology for the desired coating method (e.g. doctor blading, spraying, roll coating, screen printing, etc.). Figure 2 shows an example of the effect of pH adjustment on the viscosity of a CIGO ink used for coating. At high pH the powder surfaces are highly charged and the particles are repulsive to one another, creating a highly dispersed system and a low, Newtonian viscosity. Adjustment of the pH towards acidic conditions neutralizes some of the negative surface charge and produces an attractive particle network, and a consequently a higher, shear thinning viscosity. When the dispersion rheology is adjusted to the proper range, the ink is deposited onto moly coated soda-lime glass. This film is then annealed in a reducing atmosphere to produce a metallic phase. It is this reduction step that allows the initial powder film to fuse into a dense, compact precursor layer that is subsequently selenized. The reduced film is similar to precursor films produced by vacuum deposition techniques (sequential evaporation, sputtering) for 2-stage absorber growth, except that the surface is somewhat rougher. During the selenization process, the reaction of copper, indium and gallium with H_2Se leaves a majority of the gallium located at the rear of the absorber. Although this gallium rich phase aids in current collection by providing a back surface field, it does nothing to increase the open circuit voltage of the device. In order to open up the bandgap, films are reacted with H_2S or annealed at high temperature to diffuse gallium towards the junction.
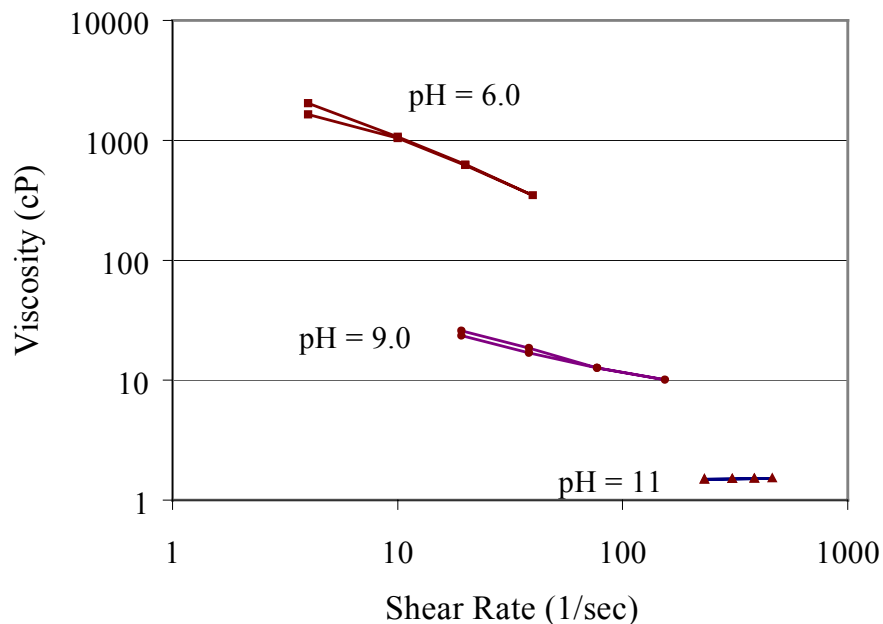

Figure 2). Plot of viscosity versus shear rate for CIO powders at various pH values.

2.2 ISET program goals and milestones

The initial Phase of the current program at ISET was geared towards the fabrication of high bandgap chalcopyrite absorbers. Vacuum deposition methods were mainly utilized for precursor film formation and the resulting absorber materials were characterized to develop an understanding of the diffusion of Ga and S. The first year of the Phase II program was focused on the extension of the sulfur and gallium inclusion efforts to the non-vacuum processing route. The e-beam evaporated films continued to see use in fundamental studies of diffusion mechanisms. Effort was concentrated on developing an understanding of sulfur and gallium distributions in films of various compositions produced by the non-vacuum process. Time was also devoted to the use of the non-vacuum deposited absorbers for the fabrication of high efficiency devices and sub-modules. Using a gallium rich phase at the Mo interface to produce a back surface field, and sulfur at the junction to increase the bandgap, device efficiencies of 13% have been achieved with selenized/sulfurized samples from non-vacuum deposited precursors. Moly has been successfully laser scribed in house and mini-modules ($A < 100cm^2$) have been fabricated with efficiencies over 8% and Voc's per cell over 480 mV (evidence of increased bandgap). Continued basic research on sulfur diffusion in e-beam deposited, Cu-rich films revealed the excess Cu-Se to be located near the back of the film, as opposed to in the front as is the case for co-evaporated films. This surprising result lead to the realization that starting with highly Cu-rich films and bringing the ratio back to near stoichiometric with Ga-Se and/or In-Se will not lead to high efficiency absorbers.

3.0 Technical Results and Discussion

3.1 Sulfur distribution studies

In Phase I of the current program, results were reported for studies on sulfur distributions in CIGSS films prepared from e-beam deposited precursors. It was determined that the nature of the S profiles in high temperature sulfurized CIGS layers was strongly dependent upon the initial CIGS stoichiometry. Sulfur distribution was found to be near uniform in Cu-rich CISS layers, with sulfur diffusion being aided by the presence of the secondary phase of Cu-Se. In near stoichiometric films, the sulfur diffusion was curtailed such that the surface concentration was highly sulfur rich, but little sulfur diffused into the bulk. Sulfur diffusion was also slower in highly In-rich absorbers but with the decreased grain size at the back resulting in a high level of sulfur at both the front and back interfaces.

In order to explain the observed sulfur diffusion phenomena, an estimate was made of the diffusion constant of sulfur in Cu-poor materials. Using near-surface S distribution data from the Auger depth profiles, and assuming a constant source of S at the surface of the film, a diffusion equation can be formulated as:

$C(x,t) = C_s \, \text{erfc} \, (x/2(Dt)^{1/2})$.

For the case of $x << 2 (Dt)1/2$, this can be simplified to:
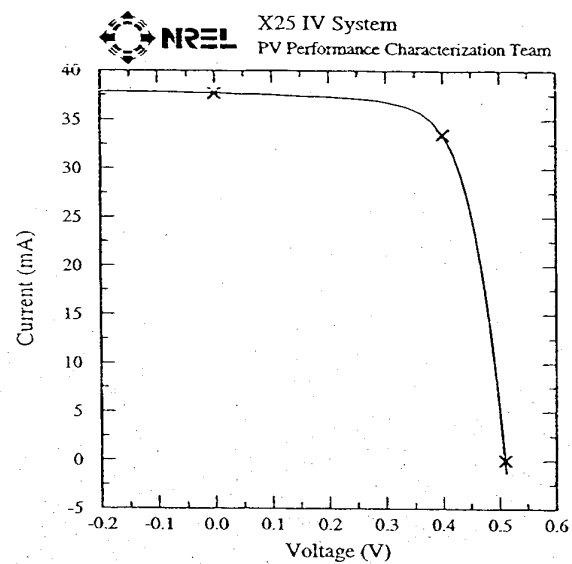
$C(x,t) = C_s \, (1-x/3.14(Dt)^{1/2})$,

and the diffusion constant D can be obtained from the slope of the $C(x,t)/C_s$ vs. x plot. Using a time of 20 minutes and x values less than 900Å, the diffusion constant was estimated to be D = $3x10^{-13}$ cm^2/sec. This result was compared to the value previously reported by the IEC group for S diffusion in slightly Cu-rich CIS (D = $1.5x10^{-11}$ cm^2/sec), to show that the S diffusion is approximately two orders of magnitude slower in Cu-poor materials. This result demonstrated the dependence of the S diffusion on the CIS stoichiometry and the consequences when attempting to form highly graded bandgap absorbers.

Additional studies were undertaken to verify the assumption used in the aforementioned calculation that the surface concentration of S is constant regardless of the initial CIS stoichiometry. Several Cu-rich and In-rich samples were annealed in H_2S and/or N_2 for 20 to 90 minutes at 475, 525 or 575°C (total time at high T was kept constant at 90 minutes and the exposure time to H_2S was varied). Plotting the surface S concentration as a function of 1/T, an activation energy can be determined that gives rise to the sulfurization of the film surface. Activation energies of 0.14eV and 0.62eV were estimated for the sulfurization of Cu-rich and In-rich surfaces respectively. The implication of this difference in activation energy is that the sulfur distributions measured in the previous study were not steady state profiles, but rather depend on the sulfurization time and temperature. Thus, calculation of the diffusion constant based on the assumption of constant surface S concentration is incorrect. Sulfur inclusion into Cu-rich surfaces is more favorable, and diffusion through a Cu-rich matrix occurs more rapidly, but additional experimentation/modeling needs to be carried out to clarify the observed phenomena.

3.2 Sulfur inclusion into materials deposited by the non-vacuum process

The majority of the work at ISET on sulfur inclusion into CIGS films has been focused on materials produced by the selenization of vacuum deposited precursors. An efficiency of 13.7% was demonstrated with a near-stoichiometric CIGSS film that was annealed at high temperature for 20 minutes under flowing H_2S. In Phase II emphasis was placed on the sulfurization of absorbers produced by the non-vacuum approach and increasing the voltage of devices without severely lowering the current collection. The focus of the most recent work was the effect of Cu/(In+Ga) and Ga/(In+Ga) ratios on the extent of sulfur inclusion and Voc increase. In the previous quarter results were reported for selenized/sulfurized samples containing Ga and produced from non-vacuum deposited precursors (Ga inclusion studies are supported by ISET's contract with the Advanced Technology Program). Efficiencies in the 11-12% range were consistently achieved using precursor inks with Cu/(In+Ga) and Ga/(In+Ga) ratios of 0.84 and 0.16 respectively. Figure 3, for example, shows the results of a device efficiency measurement conducted at NREL of an ISET CIGSS device. Auger data of similar absorbers, also taken at NREL, showed the Ga concentration to be increasing towards the back of the film as shown in Figure 4 (sulfur composition not measured). Based on the previous sulfur diffusion results from this study, it would be expected that sulfur incorporation in such a Cu-poor film

V_{oc} = 0.5097 V

I_{sc} = 0.03767 A

J_{sc} = 34.44 mA/cm^2

Fill Factor = 69.79 %

I_{max} = 33.49 mA

V_{max} = 0.4002 V

P_{max} = 13.40 mW
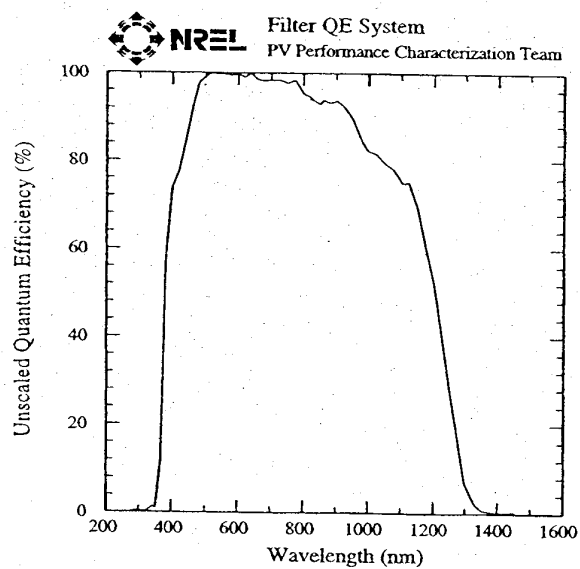
Efficiency = 12.3 %

Voltage Bias: 0.0 V

Light bias for 21.1 mA

J_{sc} Estimate:

J_{sc} (Global) = 42.6 mA/cm^2

Figure 3). I-V characteristics and quantum efficiency of a CIGSS device prepared by the ISET non-vacuum process.

would be slow and little sulfur would diffuse into the bulk of the absorber with a somewhat higher sulfur concentration near the moly interface. It is observed that after high temperature reaction with H_2S, the Voc of devices made from this precursor material increases to >500mV with very little corresponding decrease in Jsc. This suggests that the sulfur diffusion into the bulk of the CIGS is limited and only the surface region is reacting to form CISS with the gallium remaining at the Mo interface to create a back surface field. This processing scheme has resulted in devices with efficiencies exceeding 13%, with Voc values in excess of 500mV. The highest efficiency achieved thus far with materials produced from non-vacuum deposited precursors is 13.6% for a 0.087cm^2 device (efficiency measured only at ISET). A schematic representation of this I-V measurement is given in Figure 5. The measured current/voltage characteristics for this champion cell were as follows: Voc = 515mV, Jsc = 37.2mA/cm^2, FF = 70.8%.

It has been observed that selenization/sulfurization conditions (575°C, 20 minutes, 10% H_2S) that lead to high voltages and efficiencies in e-beam deposited films (Voc>550mV, η>13.5%) do not have as much of an effect on non-vacuum deposited precursors. When reduced films are selenized and sulfurized along side metallic films deposited by evaporation, the vacuum deposited films generally exhibit a higher voltage (although they may or may not be higher efficiency). Studies are being undertaken to understand this difference in the extent of sulfur incorporation between the two types of precursors in order
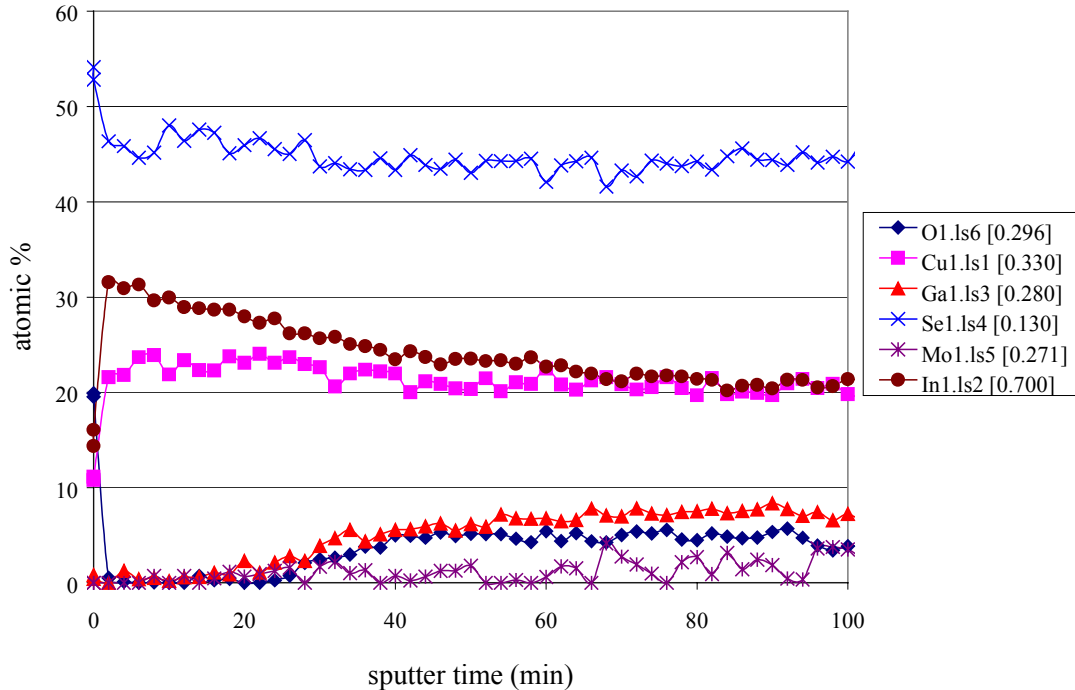

Figure 4.) Auger data of ISET sample CO1550 prepared from non-vacuum deposited precursors and showing increasing Ga content towards the back of the film.
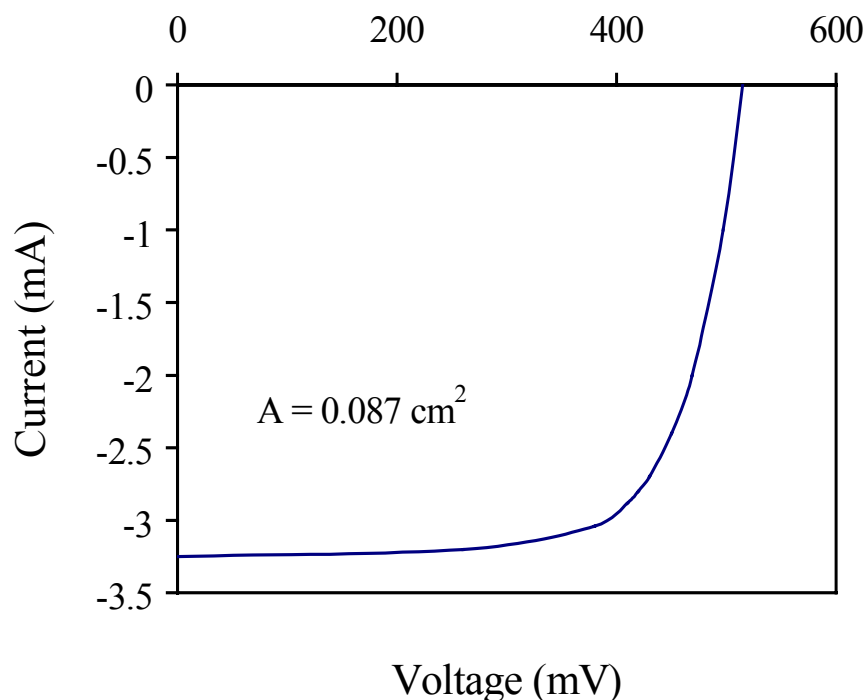
Figure 5.) Schematic of the efficiency result for ISET's champion cell: η = 13.6%, Voc = 515mV, Jsc = 37.2mA/cm^2, FF = 70.8%.

to optimize the sulfur profiles in non-vacuum processed films. There are a few distinctions between these two precursor types that could lead to a difference in open circuit voltage. Films deposited as a powder coating and subsequently reduced are generally thicker than those deposited by evaporation (2-3µ vs. 1.5-2µ). This increased thickness avoids any problems of shorting that might arise due to incomplete surface coverage of the coating. The non-vacuum precursors also frequently contain some residual oxygen left by incompletely reduced gallium or indium oxides. The microstructures of CIS films produced from the two types or precursors are similar, with the exception of a variation in surface roughness. The reduced powder films are rougher than the corresponding metal films produced by e-beam evaporation and consequently the CIS produced also exhibits a rougher surface (typically 1µ hill-to-valley for non-vacuum vs. 0.5µ for e-beam). This roughness increases the junction area, and also has some effect on gas flow across the surface and diffusion into it.

Because of the observed differences in sulfur incorporation between the non-vacuum and e-beam deposited films, more fundamental studies of sulfur profiles under various reactions conditions are necessary. Experiments have already been conducted in which the

concentration of H_2S has been varied, as well as the time and temperature profiles of sulfurization, and the effect on Voc has been measured. Recent work has emphasized varying the ratios of Cu and Ga in the precursor inks to see their effects on S inclusion. To this end, powders have been synthesized containing Cu/(In+Ga) ratios from 0.84 to 0.94, and with Ga/(In+Ga) ratios from 0.14 to 0.35. Preliminary results for the precursors with high gallium concentrations suggest that the extent of sulfur inclusion does not depend upon the amount of Ga in the film. Absorbers containing 35% Ga show similar open circuit voltages as those with 14%. Additional work needs to be carried out to measure the S distribution profiles for the non-vacuum deposited films in order to optimize the processing and achieve a graded bandgap absorber (high S concentration at junction, high Ga concentration at Mo interface). A study of the effect of increased Ga and S concentrations on the microstructure of the materials will also be initiated. A second reaction chamber has also been upgraded at ISET to include sulfurization capability and the maximum flow rate in both furnaces has been increased (maximum flow rate = 100 sccm H_2S). Analysis of the results from these S experiments should provide the information necessary to increase the open circuit voltage of non-vacuum deposited CIGSS beyond the current 480-515mV range (without significant loss of Jsc or FF).

3.3 Cu Distribution in Cu-rich Selenized Films

Auger depth profiling studies have been carried out in Phase II to understand the distribution of copper in Cu-rich (CIS+Cu-Se) selenized films. The present models for the growth of Cu-rich films by the co-evaporation technique assume the excess Cu-Se phase to be at the top surface of the film. Experimental evidence confirms this property which allows In(Ga)-Se to be deposited at the later stages of film growth and react with the Cu-rich precursor to bring the overall composition to near stoichiometric (but slightly Cu-poor). It was attempted to use such a multi-step process to grow device quality CIGS films at ISET. Cu-rich CIGS layers were fabricated by selenization of e-beam deposited precursors and In(Ga)-Se was evaporated at high temperature to adjust the composition. The results suggested that there was little intermixing between the Cu-rich bottom layer and the In(Ga)-Se top layer and the approach was not capable of producing high efficiency devices. In attempting to understand the difference in precursor films produced by this method and by co-evaporation, several Auger depth profiles were taken of Cu-rich selenized films. It was observed that the excess Cu in these films was consistently located near the Mo interface and not on top of the growing film as would be expected from co-evaporation results. Figure 6 is an example of an Auger profile of a slightly Cu-rich film formed by the selenization of a e-beam evaporated precursor. It is apparent that at about half of the film thickness, the copper concentration begins to increase while that of In and Se begin to decrease. To see if the observed Cu segregation was the same in Ga and S containing absorbers, slightly Cu-rich CIGS and CISS films were also grown and analyzed and similar results were obtained. The proposed mechanism (described below) explains how metallic precursors convert to selenides in such a way as to leave the excess Cu-rich phase at the rear of the absorber, near the Mo interface.

E-beam evaporated precursor films contain Cu-rich and In-rich alloys which convert to the stable $Cu_{11}In_9$ + In phases above 150°C. The surface region of the film is slightly In-rich, so as the temperature of the substrate is raised beyond approximately 250°C in a selenizing atmosphere, a crust of selenides is formed with a Cu-poor composition. As the temperature is raised beyond 350°C, the formation of CIS consumes most or all of the excess In within the thickening crust. The rather stable $Cu_{11}In_9$ phase is somewhat screened from the selenizing environment by the growing selenide crust and is left near the Mo interface, only to be consumed in the final stages of selenization at high temperature. Eventually the $Cu_{11}In_9$ phase releases its excess Cu to form the secondary Cu-Se phase, which is accommodated on the free surfaces of smaller grains at the Mo interface and on the boundaries of the larger grains. At Cu/In ratios of 1.2 or greater, the volume of Cu-Se phase has increased to the point where it may break through the surface crust of CIS at microscopic thickness and/or composition non-uniformities. In the present study this was observed for films with Cu/In ratios in the 1.2-1.5 range, with the area density of isolated Cu-Se grains growing with increasing Cu/In ratio. If the Cu/In ratio were further increased, eventually the excess Cu-Se phase may cover the entire surface of the CIS layer. However, this Cu segregation to the Mo interface in slightly Cu-rich precursors prevents the Cu-rich/In-rich growth method commonly used in co-evaporation scheme from being successfully utilized for high efficiency absorber growth by the selenization technique.
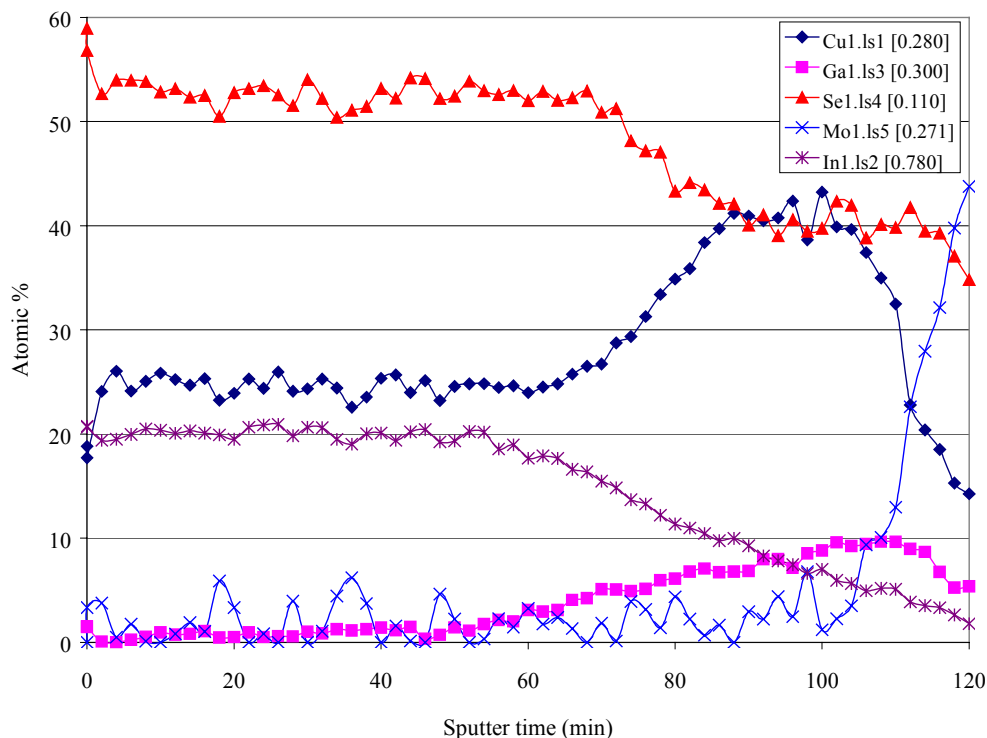

Figure 6.) Auger data of ISET sample prepared from e-beam deposited precursor and showing excess copper towards the back of the film.
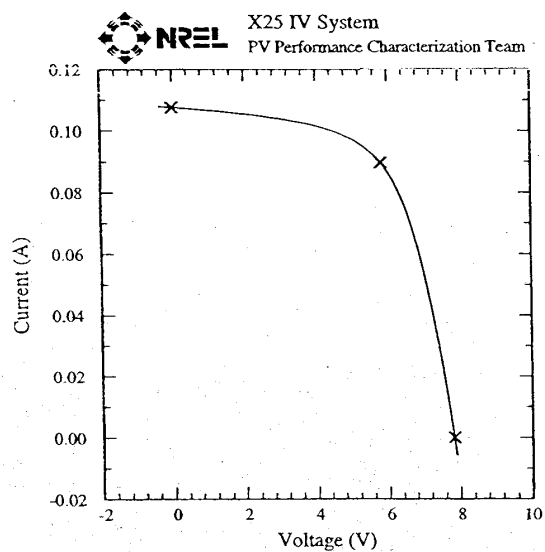
3.4 Modules/Laser Scribe

The most important task of this program is the development of high efficiency modules. In the past year, equipment has been purchased and installed to allow for moly back contact patterning with a microlaser. A 26" x 26" X-Y table manipulates the glass substrate while the laser scribes the moly for module processing. This low power laser (11mJ) is capable of producing narrow scribes approximately 25-50 microns in width in a single pass. This decreased scribe width greatly reduces the problem of de-wetting of the scribes that was commonly observed with the ink coating process on Mo scribed using photolithographic techniques. The surface chemistry of the precursor can also be manipulated to promote wetting of the scribe lines and improve the continuity of the CIS. With this microlaser in operation, sub-modules have been processed using the conventional three scribe integration scheme: laser-scribe Mo coated glass and deposit interlayer to enhance wetting, coat pn-junction materials and mechanically scribe, deposit TCO and mechanically scribe (or pattern/etch). ISET has experimented with several of these microlasers and each has shown stability problems, often after only a short period of continuos operation. The equipment is now in place to produce high efficiency modules using the new non-vacuum approach, however, frequent laser failure will require us to revert back to the previously used photolithographic method or purchase a more powerful and reliable laser.
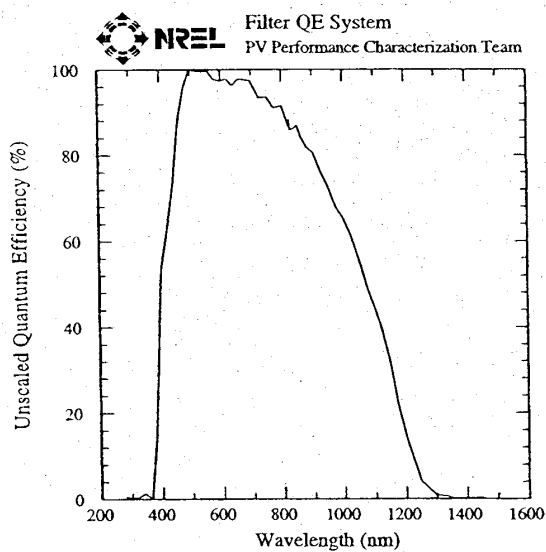
Problems with the integration process are being worked out which currently are limiting the efficiency of ISET sub-modules. Figure 7 is an example of the illuminated I-V characteristics and quantum efficiency of a recently processed CIGSS module. Although cell efficiencies are consistently in the 10-13% range over 3" x 5" pieces, the champion sub-module efficiencies have been limited to 8-8.5%. The module in Fig. 7 has an area of $65cm^2$ and gives and output of 522mW (Voc=7.84V, Jsc=1.66A, FF=61.9%, 16 cells in series). The voltage of this module is 490mV/cell but the fill factor and current are somewhat low and would improve with better integration processes. The mechanical scribing set-up does a poor job with the final isolation, severely damaging the ZnO layer. A large dead area exists between scribes on each cell, and the contact resistance is very high which lead to lower current values and poor fill factor. Continuing efforts in Phase II will attempt to improve the scribing approach, as well as developing alternative integration schemes including an all laser-scribed module and printed contacts (fewer scribes).

3.5 Large area selenization reactor

During this quarter, ISET has been upgrading its module processing capability by installing a new heating system and new gas tubing into the large area reactor that will allow both selenization and sulfurization of 13" by 13" substrates. A graphite heating system was designed and installed by Dave Bender of Bentronics. All of the necessary hardware is in place and experiments are being carried out to improve the temperature and gas flow uniformity of the system. Trial runs have been made under various selenization conditions including high and low flow rates at atmospheric pressure, high and low flow

X25 IV System
PV Performance Characterization Team

V_{oc} = 7.837 V

I_{sc} = 0.1076 A

J_{sc} = 1.658 mA/cm^2

Fill Factor = 61.89 %

I_{max} = 89.72 mA

V_{max} = 5.817 V

P_{max} = 521.9 mW

Efficiency = 8.04 %

Filter QE System
PV Performance Characterization Team

Voltage Bias: 0.0 V

Light bias for 5.77 mA

J_{sc} Estimate:

J_{sc} (Global) = 36.9 mA/cm^2

Figure 7). I-V characteristics and quantum efficiency of a CIGSS sub-module prepared by the ISET non-vacuum process.

rates under slight vacuum, and under static conditions with different amounts of hydrogen selenide. When the system is optimized, ISET will have all of the necessary equipment in place for producing 1ft^2 monolithically integrated modules.

ISET has collaborated with NREL sub-team members at the University of Florida (Prof. Tim Anderson and Suku Kim) in order to improve our understanding of the flow conditions encountered in the large area selenization reactor. A 2-dimensional model has been developed which takes into account different flow rate conditions as well as different geometries for both the reactor and the gas inlet tubes. The model is being used to determine the proper flow rate regime for optimized gas flow as well as to investigate alternative reactor configurations. Preliminary results for the current set-up explain the large non-uniformities recently observed in selenized films. The modeling clearly shows that the gas velocity over the sample in the present set-up is highly non-uniform, particularly near the center and edges of the substrate, at both low and high flow velocity conditions. Figure 8 (a, b, and c) shows the overall flow pattern, the flow speed around the gas inlet and the distribution of flow speed across the substrate for half of a sample (the model is symmetric about the center of the substrate) in the large area reactor. It is apparent that the gas velocity is near zero at the surface across a large portion of the substrate. This results in a thick boundary layer and makes the exchange of the reactant (hydrogen selenide) and reaction product (hydrogen) difficult. Using similar modeling and varying the gas flow velocity and reaction chamber geometry has resulted in suggested modifications that will result in more uniform gas flow conditions. Taking advantage of these results to modify the current set-up should improve the thickness uniformity of the boundary layer at the substrate and improve the exchange of molecules between the gas and the reaction products from the surface. With these modifications in place, the optimized large area reactor will give ISET the capability of processing 1ft^2 size monolithically integrated modules based on absorber materials from the non-vacuum process.

3.6 Alternative Buffer Layers

During Phase II, ISET has collaborated with sub-team members at the University of Florida on non-Cd containing buffer layers[2]. Several materials in the sulfide and hydroxide classes were investigated for possible replacement of CdS. Comparisons were made between ISET films, as well as Siemens Solar Industries (SSI) films, containing CdS, (CdZn)S, In(OH)$_x$S$_y$, or ZnS buffer layers (deposited at Univ. of Fla.). The films were deposited by chemical bath deposition and XPS was conducted to determine the compounds present. The In(OH)$_x$S$_y$ cell showed a lower Isc due to a lower spectral response in the long wavelength region. The relatively thick ZnS buffer layer resulted in a high series resistance and caused poor fill factor. The (Cd,Zn)S layer contained a large amount of oxygen and yielded poor current and fill factor as well as lower voltage compared to the cell with pure CdS. It was apparent that the CIGSS cell with the conventional CdS buffer layer again resulted in the best efficiency.
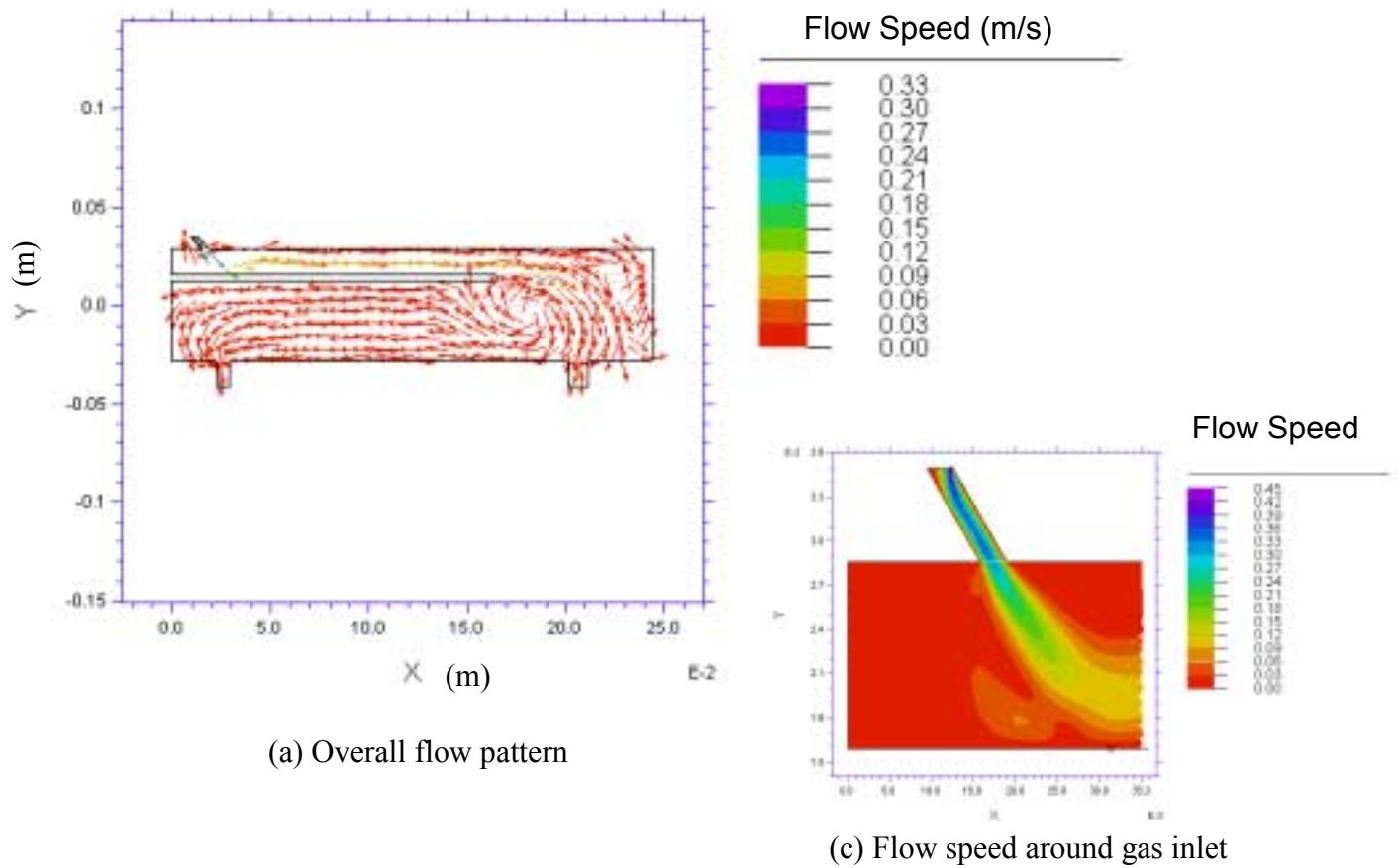
(a) Overall flow pattern
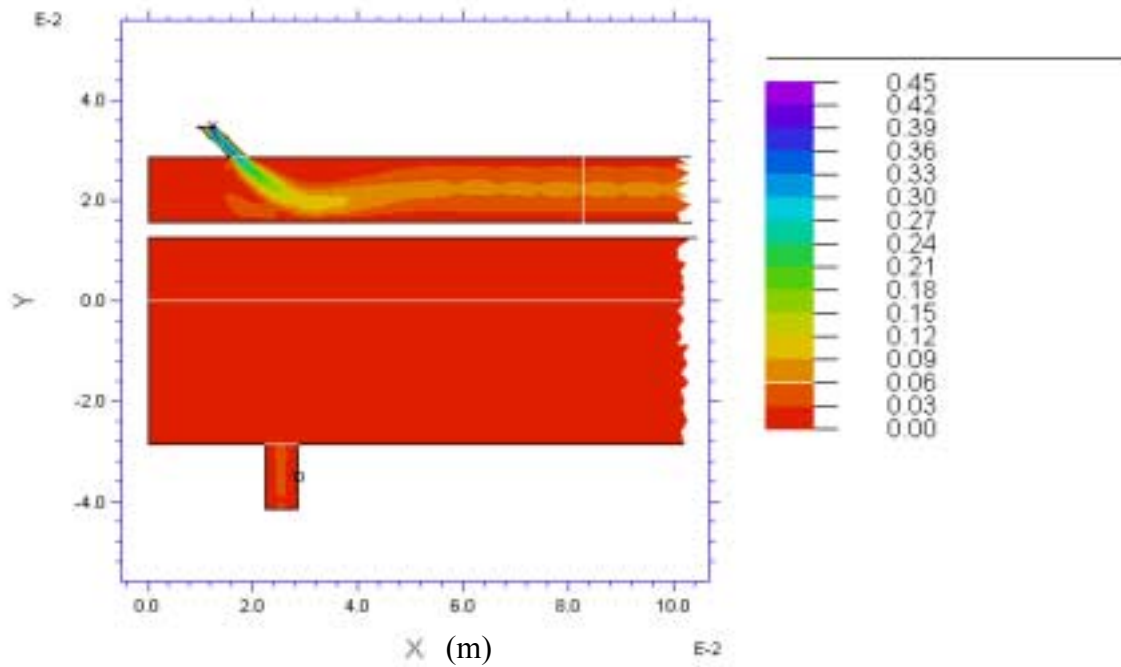
(c) Flow speed around gas inlet

Figure 8). Initial results of 2-D computer modelling being carried out at the University of Florida to optimize the gas flow uniformity in ISET's large area selenization reactor.

4.0 Future Work

Work will continue on the inclusion of sulfur into absorbers grown by the non-vacuum process. Emphasis will be placed on characterizing S and Ga compositions (Auger) as functions of Cu/(In+Ga) and Ga/(In+Ga) ratios. The goal will be to optimize the S and Ga profiles in order to increase the bandgap and improve the open circuit voltage and efficiency of devices. Temperature and gas flow uniformity will be optimized in the large area selenization reactor and fabrication of high efficiency sub-modules (12" by 12") accelerated.

5.0 Acknowledgements

6.0 References

1.   D. L. Schultz, C. J. Curtis, R. A. Flitton, H. Wiesner, J. Keane, R. J. Matson, K. M. Jones, P. A. Parilla, R. Noufi, and D. S. Ginley, "Cu-In-Ga-Se Nanoparticle Colloids as Spray Deposition Precursors for Cu(In,Ga)Se$_2$ Solar Cell Materials", *J. Elec. Materials*, Vol. 27, No. 5, (1998).

2.   C. H. Huang, S. S. Li, L. Rieth, A. Halani, J. Song, T. J. Anderson, P. H. Holloway, "Comparative Study of Chemical-bath-deposited CdS, (Cd,Zn)S, ZnS, and In(OH)$_x$S$_y$ Buffer Layers for CIS-based Solar Cells", NCPV Photovoltaics Program Review, Denver, CO, USA (2000).

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13. ABSTRACT *(Maximum 200 words)*

The R&D program at ISET is centered on development of a novel, dispersion-based route to the deposition of precursor thin films that are converted to CIS-type absorbers through high temperature reactions at or close to atmospheric pressure. The goal of the current research program at ISET is to bring a non-vacuum processing route for CIS closer to commercialization by improving the device efficiency through an increase in absorber bandgap. The basic processing approach involves first synthesizing a powder containing the oxides of copper, indium and gallium. A dispersion (ink) is prepared from the starting powder by mechanical milling or sonication. This ink is then deposited onto the glass/moly substrate as a thin precursor (3-4μm) and converted to a metallic alloy film by reaction in a hydrogen atmosphere. Controlled synthesis of starting powders and proper reduction results in reasonably smooth, metallic precursor films similar to those produced by sputtering or evaporation. From this point the processing is similar to that in the other two-stage techniques, with the metallic film being reacted in H_2Se to form the final photovoltaic absorber, followed by CdS and TCO deposition.

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